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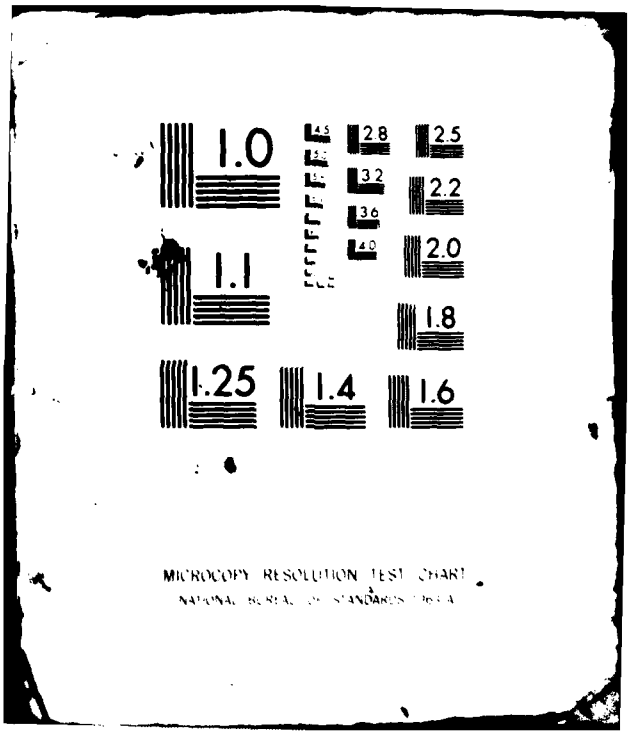
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This contract has produced a wide variety of material in the area of stiff computation resulting in nine articles that have been or will be published. In addition, five presentations have been made. This material is summarized below.

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NUMERICAL ESTIMATION IN COMBUSTION KINETICS

Final Report
AFOSR 80 0220

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February 15, 1982

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This contract has produced a wide variety of material in the area of stiff computation resulting in nine articles that have been or will be published. In addition, five presentations have been made. This material is summarized below.

PUBLICATIONS

1. "A Criterion for the Isothermal First Explosion Limit," R.C. Aiken, accepted for publication in Combustion and Flame (1981). See Appendix I for reprint.

A simple singular perturbation analysis of a combustion model yields a new and more precise description of an "explosion." Commonly used definitions held by chemists are found to be in error and that presented by the Russian Nobel Laureate Semenov found to be mathematically without rigor and very limited in scope by comparison to the completely new approach given here. In essence, Semenov's criterion for an explosion to occur can be satisfied by conditions resulting in an insignificant fuel usage to complete usage, and any intermediate degree of fuel usage. Our criterion makes the distinction among this spectrum of possible responses.

After publication in Combustion & Flame, the journal of the Combustion Institute, we hope this criterion will be useful to the combustion community to better understand the explosive kinetic activity possible under experimental conditions consistent with those used in our study. For example, it is likely that high fuel efficiency can be improved in some circumstances. We

would like to extend this thinking to more complex situations such as non-isothermal reactions or systems with continuous flow. There are many further possibilities and it all seems to me quite promising.

2. "Approximate Numerical Solutions to Explosion Kinetics," R.C. Aiken, accepted for publication in AIChE J (1981). See Appendix II for reprint.

In this article we apply this most useful approximation in the solution of ordinary differential equations -- the steady state approximations -- to combustion applications, for the first time. The reasons this approximation has not worked in the past are detailed. Basically, they have not worked because of the very stiff nature of the system in which the stiff "boundary layer" occurs internal to the solution time domain and significantly complicates the analysis.

The saved time with implementing the steady state approximation is indicated to be quite significant and has potential to allow numerical solution of real combustor models for which presently it is too time consuming to solve. Generalization is needed for kinetics equation sets of arbitrary size.

3. "Explosion Mode Analysis of an $H_2 - O_2$ Reaction," F.C. Hoppensteadt, P. Alfeld, and R.C. Aiken, submitted to Combustion Science and Technology (1981). See Appendix III.

We use here a completely new mathematical approach for the analysis of combustion dynamics in which we focus on the positive eigenvalue responsible for the explosive nature of the kinetics -- the flame "heart." An analytical solution results for the

H_2- O_2 problem, vastly reducing computation time. This approach offers real promise for more general, larger combustive systems.

4. "Numerical Treatment of Rapid Chemical Kinetics by Perturbation and Projection Methods," F.C. Hoppensteadt, R.C. Aiken, and P. Alfeld, to appear in Applied Mathematics in Chemical Kinetics, book on proceedings of meeting at University of Heidelberg (1980). See Appendix IV.

An analysis of a combustion example is performed here based on the mathematics of epidemic theory. The example is thus put into a canonical eigen-problem.

5. "Parameter Estimation in Stiff Enzyme Kinetic Systems," R.C. Aiken, to be submitted to AIChE J (1982). See Appendix V for highlights.

We focus in this article on a simple yet important reaction scheme corresponding to descriptions of enzyme action, adsorption and heterogeneous reaction, and the transition-state theory of chemical kinetics, among other examples. We first show the many ways that an approximation to the enzyme kinetics system can be made, depending on how stiffness manifests itself. This analysis goes well beyond the single conventional criterion used by biochemists. These approximations have historically been made because of the experimental difficulties of measuring intermediates that are short-lived or are present in very small concentrations. As a result of these measurement limitations, an approximation is made to eliminate the need to measure the intermediate -- with a loss, however, in the ability to estimate all

parameters associated with the original model. We used a higher approximation to the conventional approach and were able to estimate all parameters without measurements being required on the intermediate. Put another way, we were able to estimate all parameters in a set of stiff differential equations, without the need to have data in the boundary layer or to have any data on the stiff variable. Further, the equations that we had to solve were not the stiff set of ODEs but a single algebraic equation obtained from a singular perturbation analysis. The computation time required to perform a non-linear regression on a system of stiff ODEs is mostly from many repeated solutions of the stiff ODEs, so this approach is quite efficient. The main advantage, however, is that the parameters could not be estimated otherwise. Data must be accurate, however. The stiffer the system, the more accurate the data must be.

6. "Parameter Estimation in Stiff Ordinary Differential Equations," to be submitted to AIChE J. (1982).

This paper examines what can be done to improve the estimation of all parameters occurring in stiff ordinary differential equations, particularly those contributing to stiffness. No model approximations are made. This article is apparently the first to directly address this problem.

For a given model and experimental set-up, the only way we can influence the accuracy of parameter estimates is to choose the particular times at which to take data and by imposing our own weights on the data.

Consider for simplicity the linearized model equation set

$$\underline{f}_\mu = \underline{\underline{B}}_\mu(\underline{x}_\mu,\underline{\theta})\underline{\theta}$$

where $\underline{x}_\mu$ are the variables to predict (such as concentrations), $\underline{\underline{B}}_\mu$ is the Jacobian of $\underline{f}_\mu$ with respect to the parameters $\underline{\theta}$; $\mu = 1,2,..n$ represents the number of the experiment, labeled from one to n. The weighted least squares problem is to minimize

$$\Phi(\underline{\theta}) \equiv (\underline{Y}-\underline{\underline{B}}\underline{\theta})^T\underline{\underline{V}}^{-1}(\underline{Y}-\underline{\underline{B}}\underline{\theta})$$

where

$$\underline{\underline{B}}^T \equiv [\underline{\underline{B}}_1^T, \underline{\underline{B}}_2,\ldots\underline{\underline{B}}_n^T]$$

$$\underline{Y} \equiv [\underline{y}_1,\underline{y}_2,\ldots\underline{y}_n]$$

$\underline{y}_\mu$ being the observed $\underline{f}_\mu$, and $\underline{\underline{V}}^{-1}$ is the weighting matrix. For such a problem, it is well known that an "optimal" estimate $\underline{\theta}^*$ is

$$\underline{\theta}^* = (\underline{\underline{B}}^T\underline{\underline{V}}^{-1}\underline{\underline{B}})^{-1}\underline{\underline{B}}^T\underline{\underline{V}}^{-1}\underline{Y}$$

for normal distribution of measurement errors, where $\underline{\underline{V}}^{-1}$ is the inverse of the joint covariance matrix, giving an estimation variance

$$\underline{\underline{V}}_\theta = (\underline{\underline{B}}^T\underline{\underline{V}}^{-1}\underline{\underline{B}})^{-1}.$$

We wish to minimize $\underline{\underline{V}}_\theta$, in some sense.

Consider the case in which some parameters are much easier to estimate than others, as occurs with stiff kinetic problems in which the data are not optimally located or not available in all variables. We should then like to aid the computation of some parameters (at the expense of others). This could be done in a number of ways; as examples:

1. Weight matrix $\underline{\underline{V}}^{-1}$. We may choose this so that certain experiments or variables are favored in the estimation. This is the same as pretending that the data corresponding to the stiff variables (if any)are better -- or more important -- than other

data. If the stiff variables are not measured at all, the experiments with early data, for example, can be given extra importance or variables with the greatest impact on the stiff parameters can be emphasized.

2. The independent variable vector $\underline{x}_\mu$. Changes in the number and location of the data points is the only way to affect $\underline{\underline{B}}$, for a given model. This choice could be based on minimizing the $\underline{\underline{V}}_\theta$ in ways such as:

a) $\max \| \underline{\underline{B}}^T \underline{\underline{V}}^{-1} \underline{\underline{B}} \|_\infty$

b) $\max \det | \underline{\underline{B}}^T \underline{\underline{V}}^{-1} \underline{\underline{B}} |$

c) max some part of confidence region to favor certain parameters. This can be shown in the case of two parameter sets to be

$$\max \det |\Delta|$$

where

$$\Delta = Y_{11} - Y_{12} Y_{22}^{-1} Y_{21}$$

$$\underline{\underline{Y}} \equiv \underline{\underline{B}}^T \underline{\underline{B}} = \begin{bmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{bmatrix}$$

d) max sensitivity; for maximum liklihood problems with normal distribution,

$$\underline{\underline{V}}_\theta \sim \underline{\underline{H}}^{*-1}$$

where $$\underline{\underline{H}}^* \equiv \left. \frac{\partial^2 \phi}{\partial \underline{\underline{\theta}}^2} \right|_{\underline{\underline{\theta}}^*}$$

so that $\underline{x}_\mu$ can again be chosen so as to maximize sensitivity to certain parameters over others.

e) Minimization of prediction errors.

We are ultimately interested in knowing the $\underline{\theta}^*$ so as to predict $\underline{f}$ under conditions other than those of the experiments we performed. Let the observed value of $\underline{f}$ be $\underline{y}_o$ and the predicted value using $\underline{\theta}^*$ be $\underline{y}_p$; then:

$$\underline{y}_o = \underline{f}\ (\underline{\theta}^* + \delta\underline{\theta})$$

Expansion gives to a first-order approximation

$$\underline{y}_o - \underline{y}_p = \left(\frac{\partial \underline{f}}{\partial \underline{\theta}}\right)\delta\underline{\theta}$$

The covariance matrix of the prediction errors is then

$$\underline{\underline{V}}_p = \left(\frac{\partial \underline{f}}{\partial \underline{\theta}}\right)\underline{\underline{V}}_\theta \left(\frac{\partial \underline{f}}{\partial \underline{\theta}}\right)^T = \underline{\underline{B}}\underline{\underline{V}}_\theta\underline{\underline{B}}^T$$

and $\underline{\underline{V}}_\theta$ (dependent on $\underline{\underline{B}}$) can be considered a weighting matrix. Note here that the less sensitive f is to the parameters, the better the prediction.

7. "A New Method for Estimation of Rate Constants Contributing to an Explosive Reaction," to be submitted to Combustion and Flame (1982).

The conditions for explosion or for no explosion (Aiken, Aiken, et al., 1981), which involve the kinetic constants, may provide us with as many equations as we have experiments with different initial conditions. We must be able to measure at least the stable species at the inception of the explosion. Experimentally, a bomb can be charged and the temperature slowly brought up to the value producing an explosion.

8. "Review of Stiff Methods and Stiff Models 1973-1982," R.C. Aiken, to be submitted to SIAM Review (1982). We have assembled approximately one thousand stiff articles up-to-date since the Wildbad Symposium. Our search used national computerized data banks, cross referencing through the Scientific Citation Index and bibliographies sent to us by leading stiff experts. This information is programmed in our own word processor/computer for easy retrival by author, key words, etc.

We were particularly successful in assembling application areas where stiffness occurs (a helpful approach to find these articles was to look at every article quoting Gear's classic articles in recent years). These practical articles point out the needs for special methods for special problem structure, low-accuracy methods, highly automatic methods, and many others. The complete categorization of research and development in this area should be of further value.

This report will be available to participants of the International Conference on Stiff Computation, to be held at Park City, Utah, April 12, 13 and 14 and will be of use in the subsequent proceedings publication and the type-set monograph planned with Oxford University Press.

9. "Review of Modeling and Numerical Solution of Detailed Chemical Kinetics," R.C. Aiken, to be submitted to AIChE J (1982).

This article will specialize our stiff review to chemical kinetics. We address here the fundamental modeling question of how much detail is <u>necessary</u>, i.e., can we avoid solving a stiff ODE set by modeling considerations. We also focus on several

simple kinetic systems for which modeling simplifications made by notable chemists on qualitative chemical reasoning is in error.

PRESENTATIONS

1. "Steady-State Approximations During Explosions," R.C. Aiken, presented at annual AIChE meeting, New Orleans, November 8-12, 1982.

2. "Numerical Treatment of Rapid Chemical Kinetics by Perturbation and Projection Methods," F.C. Hoppensteadt, R.C. Aiken and P. Alfeld, presented at meeting on Applied Mathematics in Chemistry at the Technical University of Heidelberg, August (1980).

3. "Numerical Integration in Combustion Kinetics," R.C. Aiken, presented at Brigham Young University, Jan. 1981.

4. "Mathematical and Computational Analysis of Explosions," R.C. Aiken, presented at the University of Utah, Feb. 16, 1982.

5. "Estimation of Parameters in Stiff Ordinary Differential Equations," accepted for presentation at annual AIChE meeting, Los Angeles, November, 1982.